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**IPST Technical Paper Series Number 881**

Dual Reactive Domain Model for Sorption of Aqueous Organics by Wood Fiber

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September 2000

Submitted to  
Journal of Colloid and Interface Science

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## **Dual Reactive Domain Model for Sorption of Aqueous Organics by Wood Fiber**

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## ABSTRACT

An experimental study of 2,4,5-trichlorophenol (2,4,5-TCP) sorption to kraft papermaking fiber demonstrates that the Dual Reactive Domain Model (DRDM) effectively models the process over a broad concentration region. Isotherm data was deconvoluted into linear partitioning and nonlinear adsorption contributions in accordance with the model demonstrating the importance of both mechanisms to the overall process. DRDM accurately fit concentration dependent distribution coefficient,  $K_d(C)$ , data that could not be characterized with the Freundlich or Langmuir equations, and the model predicts the asymptotic movement towards a limiting  $K_d(C)$  value at high solute or cosolute concentrations observed in experiments. Competitive effects were accounted for by modifying the adsorption portion of the model. With its shortcomings understood, the extended Langmuir equation was utilized and provided an effective fit of data. Langmuir fitting parameters for competitive data with 5 different n-alcohol homologs allowed estimates of free energy values per methylene linkage, which were in agreement with previously reported values. Also obtained from competitive data were relative sorption values for various benzene analogs indicating that interactions in addition to those stemming from solute hydrophobicity often contribute in driving the overall sorption process. These results have implications for papermaking given the ubiquitous nature and importance of sorption in the process.

Key words: 2,4,5-Trichlorophenol, Wood, Fiber, Lignin, Sorption, Dual Reactive Domain Model, Competitive Sorption

## INTRODUCTION

Sorption of aqueous solutes to wood-fiber solids is an important component of pulping and papermaking processes. Sorption helps determine the performance of expensive wet-end additives and plays a key role in processes such as delignification, pulp washing and contaminant transport. Thus, understanding how various chemical species interact with fiber is important in controlling and optimizing the papermaking process. While there has been a considerable amount of research on the adsorption of polyelectrolytes to papermaking fiber (1-5), little has been published on neutral organic and polymer sorption or the role of hydrophobes in chemical retention (6,7). In a previous publication, results were presented for the sorption to kraft papermaking fiber by chlorophenol species (8). Data and equations from this study provide significant insight into the interactions of neutral and anionic organics with wood fiber. However, analysis of this system was limited to a narrow concentration region under dilute single-component conditions and assumed a partitioning model. In this paper, data are presented demonstrating the validity of a multiple mechanism model for describing sorption of 2,4,5-trichlorophenol (2,4,5-TCP) by kraft papermaking fiber. The model is used to fit isotherm data and extended to account for competitive sorption.

It was shown previously that under dilute conditions ( $\ll 1$  ppm), sorption of 2,4,5-TCP could be characterized using a single parameter, the distribution coefficient,  $K_d$ , defined as the ratio between the solid and aqueous phase concentrations at sorption equilibrium. This is sometimes referred to as the linear model because it supposes a linear isotherm with a slope of  $K_d$ . Use of distribution coefficients to model sorption is common for sorbents such as soils and sediments for which the process is often assumed noncompetitive.  $K_d$  values in these systems are found to correlate with

their organic carbon content indicating that sorption occurs predominately in the organic fraction (9-13). The sorption mechanism in these systems is often described as being analogous to the transfer of a solute into a lyophobic organic solvent (i.e., absorption), except in this case, the lyophobic phase consists of coiled macromolecular chains in the substrate's organic matter (14-17).

For papermaking fiber, sorption of organic species with low to moderate solubility is believed to occur predominately in the hydrophobic lignin phase, which usually comprises significantly less than 30% of the fiber mass dependent on the level of processing. Evidence for this comes from data on sorption of chlorophenols to kraft papermaking fiber of various lignin contents and sorption studies for nonpolar organic compounds using model cellulose and lignin particles (8, 18). It has also been demonstrated that chlorophenolates and likely most conjugate bases of organic acids do not participate in the sorption process (8,19). With the conjugate base having significantly higher water solubility than its acid form, e.g., 3-orders of magnitude greater for TCP, this behavior demonstrates the intuitive rule that aqueous nonpolar sorbates will preferentially sorb to nonpolar sorbents (20). For papermaking fiber, a moderate charge density due to the ionization of acid groups repels anionic species reinforcing this effect. Kraft fiber charge density ranges from 2-15 meq/100 g depending on the level of delignification (21,22). Lack of affinity for kraft fiber by the conjugate base form of 2,4,5-TCP is demonstrated in Fig. 1. Here, the sorption of 2,4,5-TCP at 100 ppb initial concentration in solution is shown as a function of pH. The measured  $pK_a$  value of 2,4,5-TCP was 6.92, which is consistent with the observed sorption demonstrating high sorption prior to this value and little if any sorption at a pH above about 9. Results of batch sorption studies were used to formulate a predictive equation of the form

$$K_d = (0.0015)\alpha K_1^0 \quad (1)$$

where  $\alpha$  and  $\kappa$  are the fraction of the chlorophenol in its acid form and kappa number of the pulp (a measure of its lignin content), respectively, and  $K_1^0$  is the lignin-water distribution coefficient for the neutral form of the chlorophenol. This last term,  $K_1^0$ , can be predicted from the solute's octanol-water distribution coefficient,  $K_{ow}$ , using a developed linear free-energy relationship (8). As will be shown later, the applicability of this simple partitioning model for papermaking fiber is limited.

Lignin in wood fiber is a complex 3-dimensional network polymer, whose characterization, for the most part, is limited to the relative amounts of various chemical linkages present (although phenyl propane is sometimes provided as a type of repeating unit) (23). The glass transition temperature of lignin is believed to be above 150°C, so it is a glassy polymer in its natural state (24). During a kraft cook, delignification reactions break linkages and introduce hydrophilic groups (primarily carboxyl groups) into the polymer causing portions to become dissolved and removed producing residual lignin of increased hydrophilicity possibly with the ability to swell. Solutes would likely have different affinities to these regions and could possibly sorb there via a different mechanism. This description is consistent with the Distributed Reactivity Model (DRM) proposed for the sorption of aqueous organics to soils and sediments (25-34). The model proposes that multiple sorption mechanisms of different reactivities can operate in parallel, and argues that differences in the reactivity are due to inhomogeneities in natural organic matter resulting from their various geologic ages. They argue that there exists 2 general types of regions in the organic matter, regions of water-swollen amorphous macromolecules and oligomers and regions of material that is more highly condensed and not swollen by the aqueous solution. Glassy and rubbery states of an amorphous polymer are offered as analogous systems for which nonlinear, competitive adsorption

and general partitioning mechanisms dominate, respectively. Differences are explained simply as increased access in the rubbery state due to its increased free volume allowing for absorption to occur more readily, while sorption in the glassy state is limited possibly in metastable equilibrium for which the movement of sorption towards an equilibrium is inhibited (35). In this paper, data are presented demonstrating the validity of the DRM approach for modeling sorption of aqueous 2,4,5-TCP to kraft papermaking fiber. More precisely, a limiting case of the DRM referred to as a Dual Reactive Domain Model (DRDM) is utilized in which 2 primary mechanisms are assumed. Results have implications for the transport and fate of chemicals in the papermaking process and possibly the design of future papermaking additives.

## MATERIALS AND METHODS

### *Materials*

Softwood pulp fiber was obtained from Georgia-Pacific Corporation. The pulp sample was thoroughly washed to remove residual processing chemicals, and the average kappa number (lignin content) was determined to be  $69.8 \pm 5$  (36). The fiber was centrifuged to 30% consistency (solids content) and stored at 5°C. The consistency of the samples was never allowed to rise above 35% to preserve the pore structure of the fibers. Non-radiolabelled solutes (all > 99% purity levels) were purchased from Chemservices (West Chester, PA) and stored as received at 2°C. The [ $^{14}\text{C}$ ] 2,4,5-TCP (4.40 mCi/mmol) was purchased from Sigma Chemical Company (St. Louis, MO) at a >99% purity as determined by HPLC. It was stored in an amber vial as a concentrated methanol solution at 2°C. Scintillation counting was done on a Beckman (Fullerton, CA) Model LS 3801 Scintillation Counter. Scintiverse E Scintillation Cocktail (Fisher, Pittsburgh, PA) was used for all solution phase samples, and Sigma-Fluor™ Universal LSC Cocktail was used with the fiber samples.



### *Determination of Acid Dissociation Constants*

The conjugate base of 2,4,5-TCP had significantly different absorption spectra from that of its acid forms, which allowed their  $pK_a$ s to be determined spectrophotometrically (37). Spectra were taken on a Perkin-Elmer (Norwalk, CT) Lambda 4B UV/VIS instrument. At 25°C,  $pK_a = 6.92 \pm 0.02$  for 2,4,5-TCP in distilled water adjusted for pH with weak HCl and NaOH solutions. For all sorption measurements, pH was carefully controlled and monitored. The ability of cosolutes used in this study to change the  $pK_a$  of 2,4,5-TCP was tested by measuring  $pK_a$  values in their presence. Measurements at their highest concentration used in competitive sorption studies demonstrate no effect on the  $pK_a$  of 2,4,5-TCP.

### *Sorption Experiments*

Twenty mL of a weak aqueous buffer (pH = 7.00) were combined with 50 mg (oven-dried) of fibers in amber vials with Teflon lined caps. 2,4,5-TCP (46.7 nCi) was introduced as well as unlabelled cosolutes for competitive studies. Time course measurements showed 4 days was more than sufficient for equilibration. Following equilibration, the solution was vacuum filtered using 0.1  $\mu$ m pore size Anopore™ Inorganic Membranes (Alltech, Deerfield, IL) and placed into a 20-mL scintillation vial. Triplicate measurements of 2,4,5-TCP concentration in the separated aqueous filtrate were made and quench corrected using chemical quench curves generated from  $^{14}\text{C}$  standards (Beckman, Fullerton, CA). Chlorophenols associated with the fiber were leached out by adding 4.32 mL of both water and methanol, 180  $\mu$ L of acetic acid (to reduce chemiluminescence), and an aqueous scintillation cocktail (12 mL) to the fibers in a scintillation vial. The mixture was agitated and allowed to settle over 4 days. The vial was then counted and the counts quench

corrected using standards containing varying amounts of fiber. Overall mass balances were between 98.4 and 100%.

It was difficult to obtain an accurate dry weight of the fibers taken for counting. Water constitutes a substantial ( $\approx 65\%$ ) and variable part of the fiber mass, and it was, therefore, necessary to directly measure the weight of the fibers counted. Fortunately, the degree of quench was sensitive to the fiber mass added. Standard plots of the quench factor (H number) vs. the amount of dry fiber added were linear ( $r^2 \geq 0.97$ ), and the weight of the fiber transferred for counting in the sorption experiments could be directly obtained from the amount of quenching (38). Measured distribution coefficients had an uncertainty of less than  $\pm 3$  mL/g.

### *Data Analysis*

Nonlinear regression was performed using curve-fitting software, DataFit, available from Oakdale Engineering (Oakdale, PA). DataFit performs nonlinear regression using the Levenberg-Marquardt method with double precision. Results were used to determine the uncertainty in fitting parameters reported at a 95% confidence level.

## **RESULTS AND DISCUSSION**

### *Single Component Isotherm Data*

Figure 2 is a 25°C isotherm for the sorption of 2,4,5-TCP to a kappa number 68.9, kraft softwood fiber plotted over a concentration range of 10 ppb to 5 ppm (initial concentration in solution). A linear least-squares fit of the isotherm forced through the origin provides a decent fit of the data ( $r^2 = 0.981$ ). However, with the aid of the plotted line, it can be seen that the isotherm data are

clearly nonlinear. This is demonstrated more explicitly in Fig. 3 with a plot of the “concentration-dependent” distribution coefficient,  $K_d(C)$ . The concentration-dependent distribution coefficient is defined as the ratio of the solid ( $C_s$ ) and solution ( $C_w$ ) phase equilibrium concentrations of 2,4,5-TCP for a specified aqueous-phase concentration (solute or cosolute). The figure shows that  $K_d(C)$  decreases as solute concentration is increased moving in an asymptotic fashion towards a limiting value. It is apparent from the expected behavior of the distribution coefficient marked on Fig. 3 that a linear model may only be accurate under very limited circumstances.

Attempts to account for the saturation or nonlinear behavior of sorption led to the use of the Langmuir and Freundlich Equations, Eqs. [2] and [3], respectively.

$$C_s = \frac{bC_s^{\max}C_w}{1 + bC_w} \quad (2)$$

$$C_s = K_f C_w^n \quad (3)$$

Figure 2 shows the use of the Langmuir equation to fit the isotherm data. Constants  $C_s^{\max}$  and  $b$  are measures of the substrate’s sorbent capacity and affinity (related to free energy) for the substrate, respectively. The Langmuir equation can be derived for highly restricted conditions for which few systems comply, but the equation is commonly used to fit nonlinear isotherm data. Its successful use is often used as evidence for approximate homogeneity of sorption sites. It appears to provide an accurate fit of isotherm data ( $r^2 = 1.00$ ). Rearranging Eq. [2] to a form that includes  $K_d(C)$ , i.e.,

$$K_d(C) = \frac{bC_s^{\max}}{1 + bC_w} \quad (4)$$

allow its use in fitting the data of Fig. 3. Although the correlation coefficient is above what might be considered an acceptable level, it is obvious from the figure that Eq. [4] cannot accurately fit the data. In addition to eliminating the Langmuir Equation as a model for the system, these results also appear to indicate that in some circumstances,  $K_d(C)$  is a more sensitive gauge of a model's ability to fit experimental isotherm data.

The Freundlich equation is a frequently utilized model for fitting isotherm data for the sorption of aqueous organics to organic phases. Although it is often described as being an empirical equation, it has been demonstrated that the Freundlich model is consistent with various proposed mechanisms including a multi-mechanism DRM approach (25-34). It can conservatively be said that an accurate fit using the Freundlich equation is consistent with a heterogeneous substrate. Constants  $K_f$  and  $n$  can roughly be thought of as measures of a substrate's capacity for a solute and intensity of adsorption, respectively. Like the Langmuir model, the Freundlich equation provides an excellent fit of isotherm data in Fig. 2 ( $r^2 = 0.999$ ), but cannot accurately fit the concentration-dependent, distribution coefficient data in Fig. 3. (In its  $K_d(C)$  form Eq. [3] is unchanged. It would just be expected that the  $n$  value measured would be 1 minus the  $n$  value determined from isotherm data.)

As mentioned previously, DRDM is a limiting case of DRM. It considers two contributions to the sorption process, one that accounts for noncompetitive partitioning behavior using a distribution coefficient and one accounting for saturating, competitive behavior using the Langmuir equation, i.e.,

$$C_s = K_d C_w + \frac{\alpha b C_s^{\max} C_w}{1 + \alpha b C_w} \quad (5)$$

The acidity constant,  $\alpha$ , is included to account for the ionization of 2,4,5-TCP.  $K_d$  is a constant that characterizes the true partitioning that is occurring in the system. If the value of this constant is known, subtracting  $K_d C_w$  from both sides of the equation can isolate adsorption behavior. Figure 4 illustrates the overall isotherm and its linear and nonlinear components of Eq. [5]. The distribution coefficient for the fit of the equation was found by linearizing Eq. [5], and minimizing the variation in the Langmuir constants for  $K_d$  over the full concentration covered by the isotherm data. This process produced a value of 27.0 mL/g, which was used to fit the data. Equation [5] can be rearranged to its concentration dependent distribution coefficient form, i.e.,

$$K_d(C) = K_d + \frac{\alpha b C_s^{\max}}{1 + \alpha b C_w} \quad (6)$$

This equation was used to fit the  $K_d(C)$  data that could not be accurately fit by the other models.

Results are shown in Fig. 5. The values found for constants  $C_s^{\max}$  and  $b$  were  $0.000582 \pm 0.0000330$  mmol./g and  $132,000 \pm 11,400$  mL/mmol., respectively.

### *Competitive Isotherm Data*

Competitive sorption will occur where sorption sites are limited, thus should only impact the adsorption portion of the mechanism described by Eq. [5]. One method for checking this is to swamp the interface with a cosorbate to determine if the sorption of 2,4,5-TCP drops to its  $K_d$  limit value. Figure 6 is a plot of the distribution coefficient for the sorption of 2,4,5-TCP by kraft papermaking fiber (kappa number 69.6). Here, 2,4,5-TCP was introduced to a solution at a concentration of 100 ppb, and its distribution coefficient is plotted as a function of cosolute

concentration. The cosolute in Fig. 6 is 2,4,6-trichlorophenol (2,4,6-TCP), a structural isomer of 2,4,5-TCP. At a pH of 7.00, the curve levels off close to 27 mL/g. (The same value found from isotherm data.) Dividing this value by the fraction of 2,4,5-TCP in its acid form at pH 7.00 ( $\alpha = 0.454$  using measured  $pK_a$  value of 6.92), the sorption of the acid form of the compound can be estimated. The estimated value is 59.4 mL/g. Measured values of  $K_d(C)$  for 2,4,5-TCP for a solution saturated in 2,4,6-TCP at pH of 2.00 averaged 60.1 mL/g, in close agreement with the predicted value. To the best of our knowledge, the validity of the DRDM model has not been demonstrated in such a direct fashion previously.

Equation [6] can be augmented to account for competitive adsorption. One approach for doing this is to extend the Langmuir (adsorption) portion of the DRDM. For the sorption of 2,4,5-TCP in the presence of  $n$  aqueous cosolutes competing for a homogeneous set of adsorption sites, the multi-component extension using the Langmuir Equation takes the form

$$K_d(C) = K_d + \frac{\alpha C_s^{\max} b}{1 + \alpha b C_w + \sum_{i=1}^n \alpha_i b_i C_{wi}} \quad (7)$$

Here, the unmarked constants are for 2,4,5-TCP, and the subscripts are used for other cosolutes.

The Langmuir Equation often does not accurately fit single component isotherms and its extended form is said to be thermodynamically inconsistent due to the requirement that the substrate possess the same capacity for all sorbates (39). Thus, its use in describing multicomponent sorption is often avoided. However, for this particular system it was found to provide an excellent description of competitive processes. From a pragmatic point of view, Eq. [7] has merit simply because it is effective at describing competitive sorption of aqueous organics to fiber, where no description was previously available. For example, Fig. 7 shows the

experimental and predicted using Eq. [7] and the parameters from the fit of the 2,4,5-TCP (single-component) isotherm data. (Assuming the isomers 2,4,5-TCP and 2,4,6-TCP have the same affinity for the fiber.) However, it is understood that there are likely limitations to this approach (40). Its success here is a result of an excellent fit by the Langmuir Equation for the adsorption portion of the single-component isotherms, and because in the case of 2,4,6-TCP and 2,4,5-TCP, the substrate likely has the same capacity for the solutes. As demonstrated below, the approach also appears to be applicable to the smaller n-alcohol homologs and benzene analogs, which are relatively close to each other in molecular weight.

Figure 6 shows the sorption of 2,4,5-TCP at 100 ppb (initial concentration) as a function of cosolute molar concentrations. The cosolutes in this case are the normal alcohol homologs methanol, ethanol, propanol, butanol and pentanol. The alcohols decrease sorption of 2,4,5-TCP, and the more hydrophobic (or less hydrophilic) the alcohol, the more sharply sorption decreases. This demonstrates Traube's Rule, which essentially says that sorption of organic species increases strongly and in a regular fashion as you ascend a homologous series (20). In other words, the decrease in sorption is assumed to be a result of alcohol adsorption that competes for sites and is at significantly higher concentrations than 2,4,5-TCP (around 5 orders of magnitude higher), and the higher the species activity in water the greater its sorption. This data can be fit with Eq. [7] by noting that the concentration of 2,4,5-TCP is a tiny fraction of the alcohol concentration used in each experiment. These conditions were not chosen to simply test the validity of the equation. In practice, the sorption of organic species to wood fiber occurs in a complex slurry of materials. Most of the solutes present are highly water-soluble and have low affinities for fiber surfaces, while species such as additives or contaminants are added or

produced at low levels. Under these conditions Eq. [7] reduces to a form that only includes the concentration of the alcohol,  $C_{wi}$ , i.e.,

$$K_d(C) = K_d + \frac{\alpha C_s^{\max} b}{1 + b_i C_{wi}} \quad (8)$$

The alcohol concentrations used in fitting the equation are their initial solution phase concentrations. This is justified by the fact that the affinity of alcohols for the fiber is so slight, producing negligible change in the solution phase concentration. In fact, measuring the sorption of alcohols would be impossible if it were not for an indirect method described here. Nonlinear, least-squares fits of Eq. [8] using a  $K_d$  value of 27.0 mL/g is shown in Fig. 7, and determined Langmuir constants are shown in Table I. Values for the product of  $\alpha$ ,  $C_s^{\max}$  and  $b$  are in close agreement with the value determined from the 2,4,5-TCP isotherm of  $34.8 \pm 1.35$  mL/g.

Assuming the system adheres to the assumptions of the Langmuir model. The constant  $b$  is related to the free energy of adsorption,  $b(\text{mL}/\text{mmol.}) = V \exp(-\Delta G^\circ/RT)$  near room temperature where  $V$  is the molar volume of water (55.3 mL/mmol.),  $T$  is absolute temperature,  $R$  is the gas constant and  $\Delta G^\circ$  is the free energy of adsorption at infinite dilution (40). Thus, the difference between the value  $-RT \ln b_n$  for a homolog with  $n$  methylene linkages and the  $-RT \ln b_0$  value for methanol should be the free energy contribution from  $n$  methylene linkages ( $n\Delta G^\circ_{-\text{CH}_2-}$ ), i.e.,

$$-RT \ln b_n = n\Delta G^\circ_{-\text{CH}_2-} - RT \ln b_0 \quad (9)$$

Figure 8 shows the linear fit of  $-RT \ln b_n$  vs.  $n$  data. The slope of this line is  $2.01 \pm 0.301$  kJ/mol. This is within the range of values previously reported for the transfer of methylene linkages out of water to a second phase, which is broad ranging from about 0.75 kJ/mol. for the enhanced sorption of alkyl amines to charged surfaces (41) to 3.6 kJ/mol. for the water solubilization of  $n$ -



alcohols (42). It has been suggested that values falling short of the water-solubilization free energy of methylene linkages are indications of only a fractional relief from hydrophobic interactions (43). So, in the sorption of methylene linkages of n-alcohols to the lignin in wood fiber, there would be approximately a 56% relief from free energy arising from hydrophobic interactions. Also shown in the plot, but not used in the fit is benzyl alcohol. It has been estimated that a phenyl ring is equivalent to about 3.5 methylene linkages in terms of free energy of adsorption (44), thus an  $n$  value of 4.5 was used. As can be seen, it does not fall on the same line as the normal alcohol homologs, possibly indicating interactions other than hydrophobic (e.g., hydrogen bonding) play a role in the sorption process.

Another correlation that offers insight into the process is that between  $-\log b$  and the log of the species octanol-water distribution coefficient ( $K_{ow}$ ). The log of a molecule's octanol-water distribution coefficient has been found to correlate with a number of properties related to its transfer between an aqueous solution and a second phase (e.g., pure solute, organic matter in soils and sediments) (45,46). The success of these types of correlations is often held as evidence for the participation of solution phase interactions in driving the process. In Fig. 9,  $-\log b$  of the normal alcohol homologs is plotted against their octanol-water distribution coefficients. Again, a linear fit is found with a correlation coefficient of 0.993. Also on the plot are the  $-\log b$  values for benzyl alcohol and various substituted benzenes including benzaldehyde, toluene, benzoic acid and 2,4,5-TCP. These species are all from different chemical families, but share the trait of a phenyl ring in their structure. Measurements of  $b$  for these species were made in ways that make Eq. [8] approximately valid. For example, given its expected high affinity for the fiber phase and lack of an ionizable functional group, several low concentration measurements were

used to estimate  $b$  for toluene. Benzoic acid showed no competition with 2,4,5-TCP at pH 7.00, which would be expected given its low  $pK_a$  value of 4.19 at 25°C. For this molecule, several low concentration measurements were made at a pH of 2.00, and those constants were used for the higher pH conditions. Given the chemical differences, it would not be expected that these species would produce a line as the homologs do. However, as can be seen, certain divisions and trends appear to be forming. It is well known that if the capability for hydrogen bonding exists, sorption is increased, and aromatic functional groups tend to enhance sorption relative to the aliphatic groups with the same solvophobicity. These rules are demonstrated here with three groupings, n-alkanes, benzene analogs with little hydrogen bonding capability and those with greater hydrogen bonding capability.

Figure 10 again demonstrates the applicability of Eq. [7]. This is the aqueous sorption of 2,4,5-TCP at a 100 ppb initial concentration as a function of the concentration of a mixture of 13 phenolic compounds. All of the species in the mixture have the same mass concentration, which is the domain value given. The mixture includes 4-chloro-3-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, phenol, 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol. This system contains an array of chemistries ranging in water solubility and ionization, which is more representative of what would be found in process streams at a pulp mill. Again, the concentrations of the cosolutes are such that the term containing the concentration of 2,4,5-TCP can be neglected from Eq. [7]. It is also assumed that the sorption of each of these species is small enough that their equilibrium and initial aqueous phase concentrations are approximately the same. Given the conditions these sorption

experiments were run, this is a fair assumption. For example, consider that sorption of 2,4,6-TCP, which possesses one of the higher affinities of those tested for the fiber phase. Its solution phase concentration changes by less than 2% in the sorption process. With these assumptions, Eq. [8] can be written as

$$K_d(C) = K_d + \frac{C_s^{\max} b\alpha}{1 + C_{wi}^{\max} \sum_{i=1}^{13} \frac{b_i \alpha_i}{M_i}} \quad (10)$$

Here, molar concentration of the  $i^{\text{th}}$  species has been replaced by its mass concentration divided by its molecular weight  $M$ . Figure 10 shows the fit of the data using Eq. [10]. Again, the measured  $C_s^{\max} b\alpha$  value of  $34.5 \pm 1.36$  mL/g is in agreement with values measured previously for competitive and noncompetitive sorption.

## SUMMARY AND CONCLUSIONS

Data presented here demonstrate the validity of the Dual Reactive Domain Model (DRDM) in describing the sorption of aqueous 2,4,5-TCP to kraft papermaking fiber. Although linear, Freundlich, Langmuir and DRDM equations all provide seemingly acceptable fits of single-component isotherm data, only the DRDM is able to accurately characterize sorption behavior over a broad concentration region. This is evident from attempts to fit isotherm data in its concentration dependent distribution coefficient,  $K_d(C)$ , form, and from the shape of  $K_d(C)$  curves in which a cosolute is added at high concentrations to dominate competitive interactions. By rearranging the model into a form explicit in  $K_d(C)$  (Eq. [6]), behavior sometimes labeled as anomalous can be explained, specifically behavior consistent with partitioning at dilute and saturating concentrations. The model separates partitioning and adsorption contributions

allowing it to be augmented for competitive effects by modifying only the adsorption portion of the equation. Given that adsorption is modeled with the Langmuir equation, use of the extended Langmuir equation was used in an initial attempt to account for adsorption competition. This was effective for all chemicals tested. Data on the normal alcohol homologs demonstrates the dominating role even highly soluble materials can play if their concentrations are high enough, while results for various benzene analogs indicate interactions other than hydrophobic are participating in driving the adsorption process. Results presented here have a number of practical implications. Possibly the most significant being that single-component isotherm data provide a poor indication of chemical retention under process conditions. Paper process streams are rich in soluble organic material that likely saturates adsorption sites limiting sorption to the partitioning mechanism but not eliminating it. Future work will examine the long-term time dependency of the model and sorption to hydrophilically modified lignin in attempts to better understand the nature of the mechanism.

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## FIGURE LEGENDS

Figure 1. Sorption of 2,4,5-TCP (100 ppb initial concentration) to kappa number 69.8 kraft papermaking fiber as a function of pH. The solid curve is the predicted sorption assuming the chlorophenolate form of 2,4,5-TCP is not retained by the fiber.

Figure 2. Single-component isotherm data for the sorption of 2,4,5-TCP to kappa number 69.8 kraft papermaking fiber at 25°C and pH 7.00. Attempts to fit the data with the Linear, Freundlich and Langmuir Equations are shown.

Figure 3. Concentration-dependent distribution coefficient,  $K_d(C)$ , as a function of equilibrium solution-phase concentrations,  $C_w$ , for the sorption of 2,4,5-TCP to kappa number 69.8 kraft papermaking fiber at 25°C and pH 7.00. Attempts to fit the data with the Linear, Freundlich and Langmuir Equations are shown.

Figure 4. Fit of single-component isotherm data for the sorption of 2,4,5-TCP to papermaking fiber using the Dual Reactive Domain Model (DRDM). Also shown are the deconvoluted linear and nonlinear (Langmuir) components.

Figure 5. Fit of  $K_d(C)$  vs.  $C_w$  data for the sorption of 2,4,5-TCP to papermaking fiber using the DRDM.



Figure 6.  $K_d(C)$  values for the sorption of 2,4,5-TCP to papermaking fiber as a function of added 2,4,6-TCP concentrations. The solid curve is the predicted behavior using parameters from the single-component isotherm for 2,4,5-TCP.

Figure 7.  $K_d(C)$  values for the sorption of 2,4,5-TCP to papermaking fiber as a function of added n-alcohol concentrations. The solid curve is the best fit of the data using DRDM.

Figure 8. Free energy of adsorption for dilute concentrations from the Langmuir model ( $-RT \ln b$ ) for sorption of n-alkanes and benzyl alcohol to kappa number 69.8 kraft papermaking fiber. Parameter b for alcohols was determined by fitting data with a competitive Langmuir model.

Figure 9. Plot of  $-\log b$  vs.  $\log$  of the octanol-water distribution coefficient,  $K_{ow}$ , for various organic species. The parameter b was determined by applying the competitive Langmuir model.

Figure 10.  $K_d(C)$  values for the sorption of 2,4,5-TCP to papermaking fiber as a function of added mix concentrations (see text). The solid curve is the best fit of the data using DRDM.

## TABLES

TABLE I. Fitting parameters for the fit of  $K_d(C)$  vs. added n-alcohol concentrations using Eq [8].

Cosorbate	$C_s^{\max} b\alpha$ (mL/g)	b (mL/mmol.)	$r^2$
Methanol	$35.6 \pm 2.39$	$0.670 \pm 0.167$	0.951
Ethanol	$36.5 \pm 1.16$	$1.58 \pm 0.182$	0.989
Propanol	$35.3 \pm 1.98$	$4.39 \pm 0.740$	0.987
Butanol	$34.5 \pm 0.888$	$9.06 \pm 0.995$	0.995
Pentanol	$33.3 \pm 2.54$	$18.2 \pm 4.89$	0.942

## FIGURES

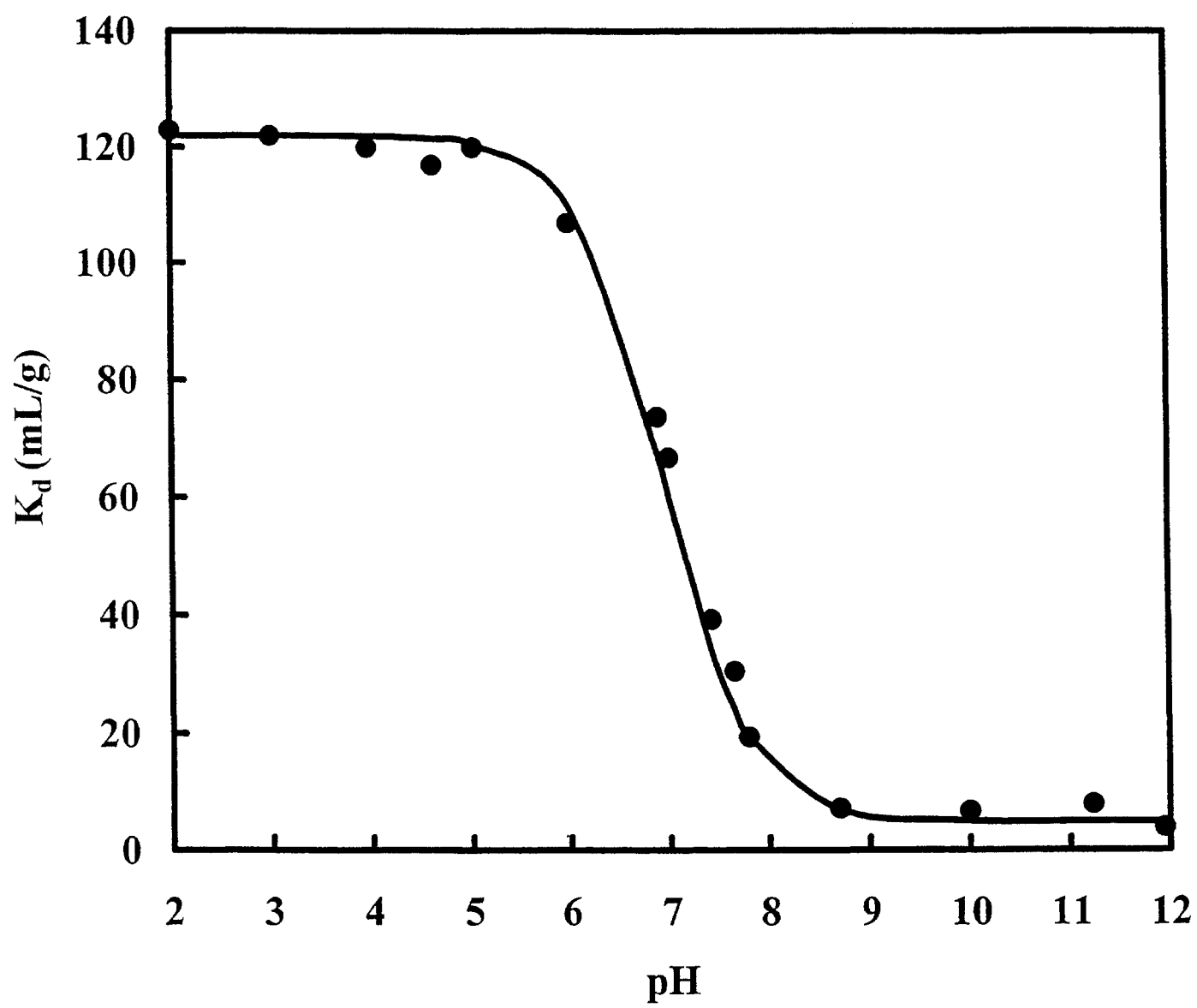


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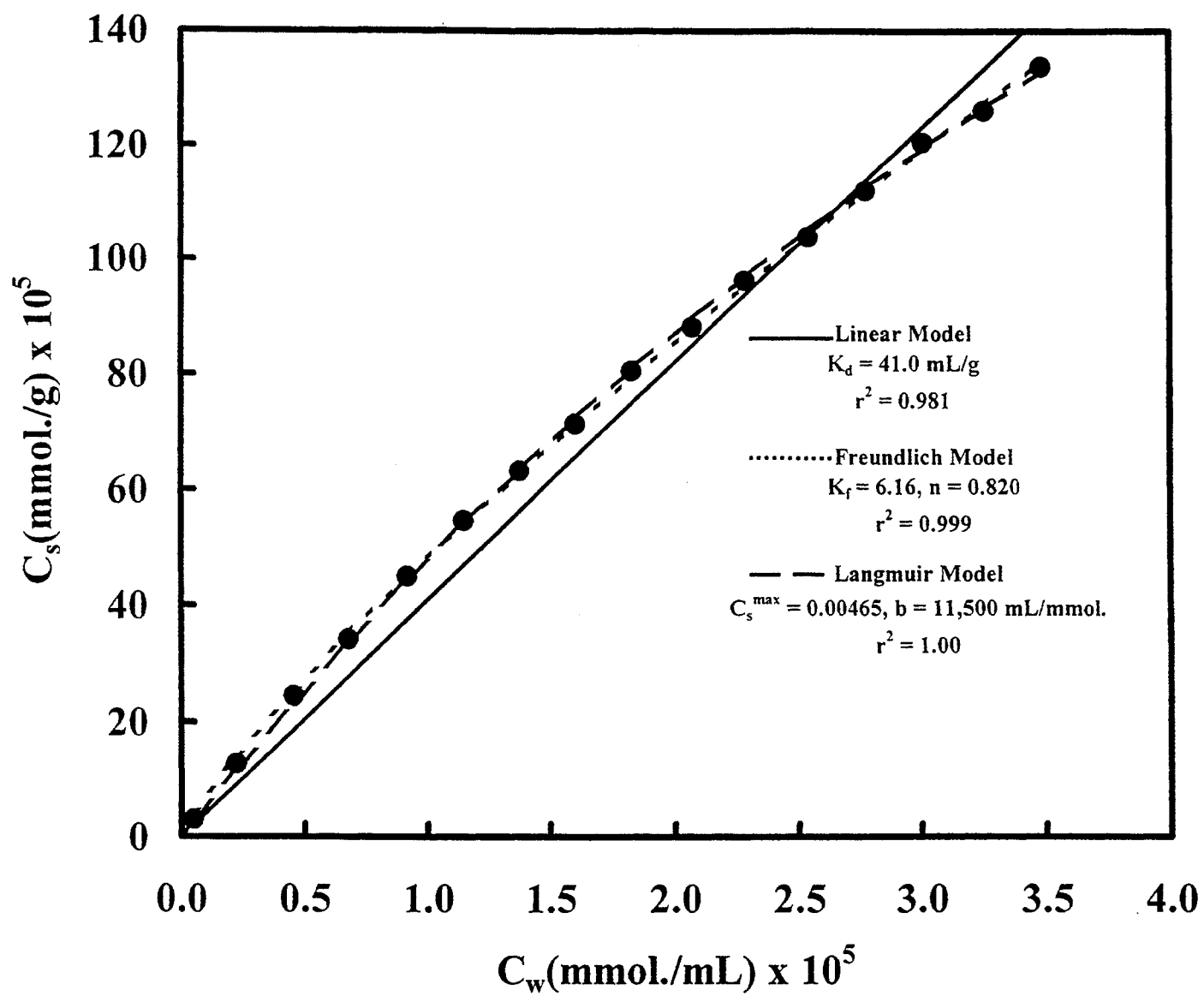


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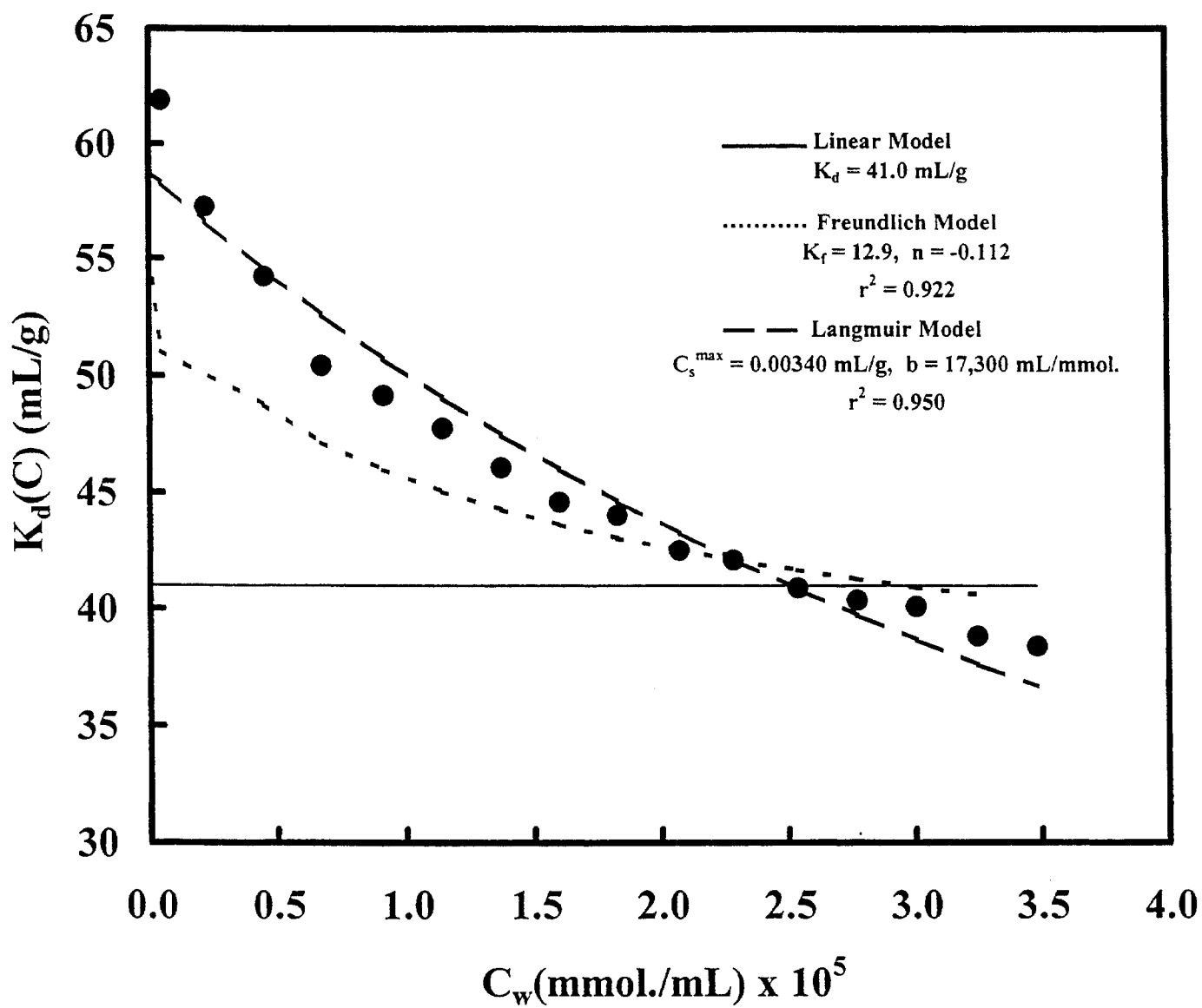


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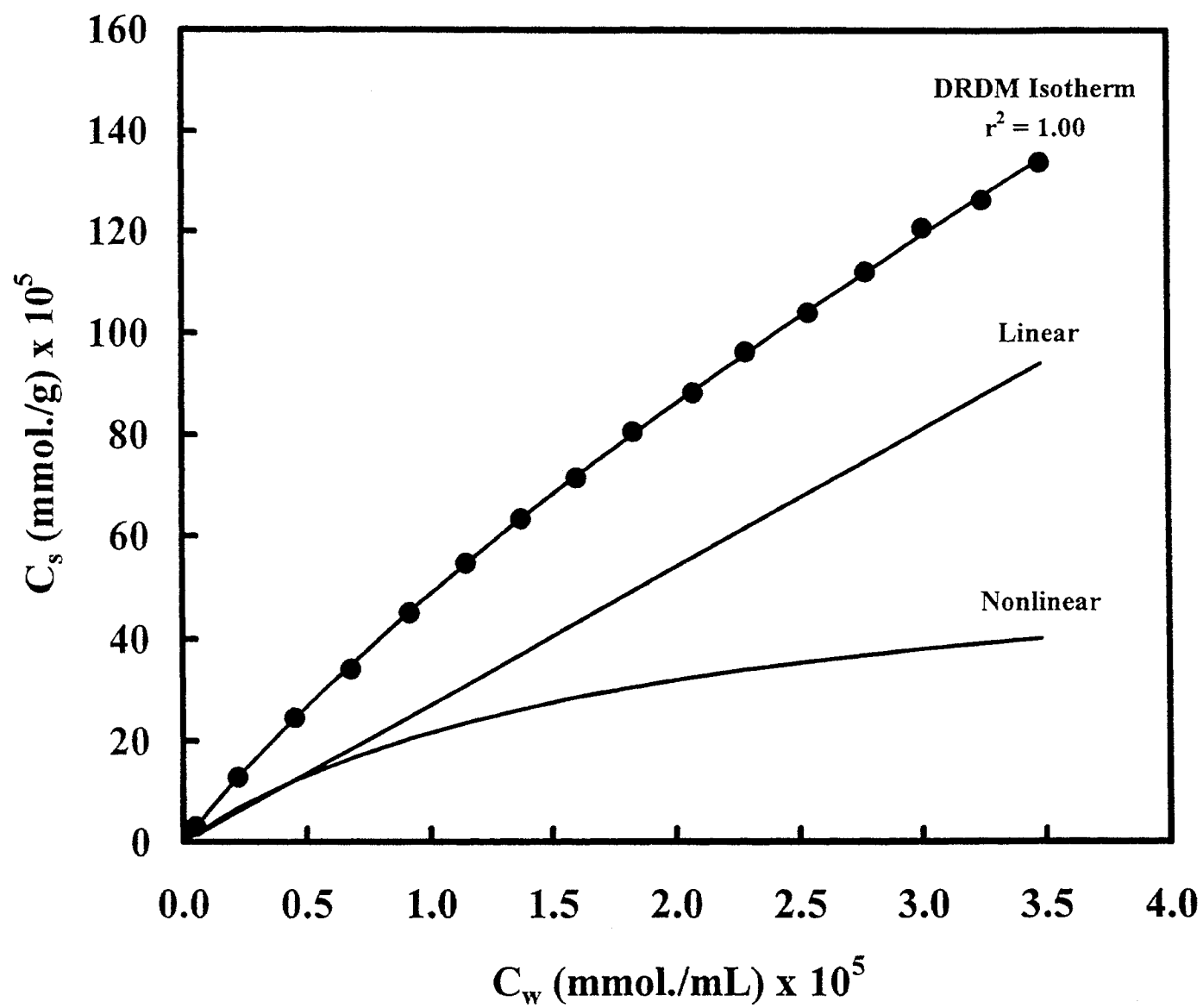


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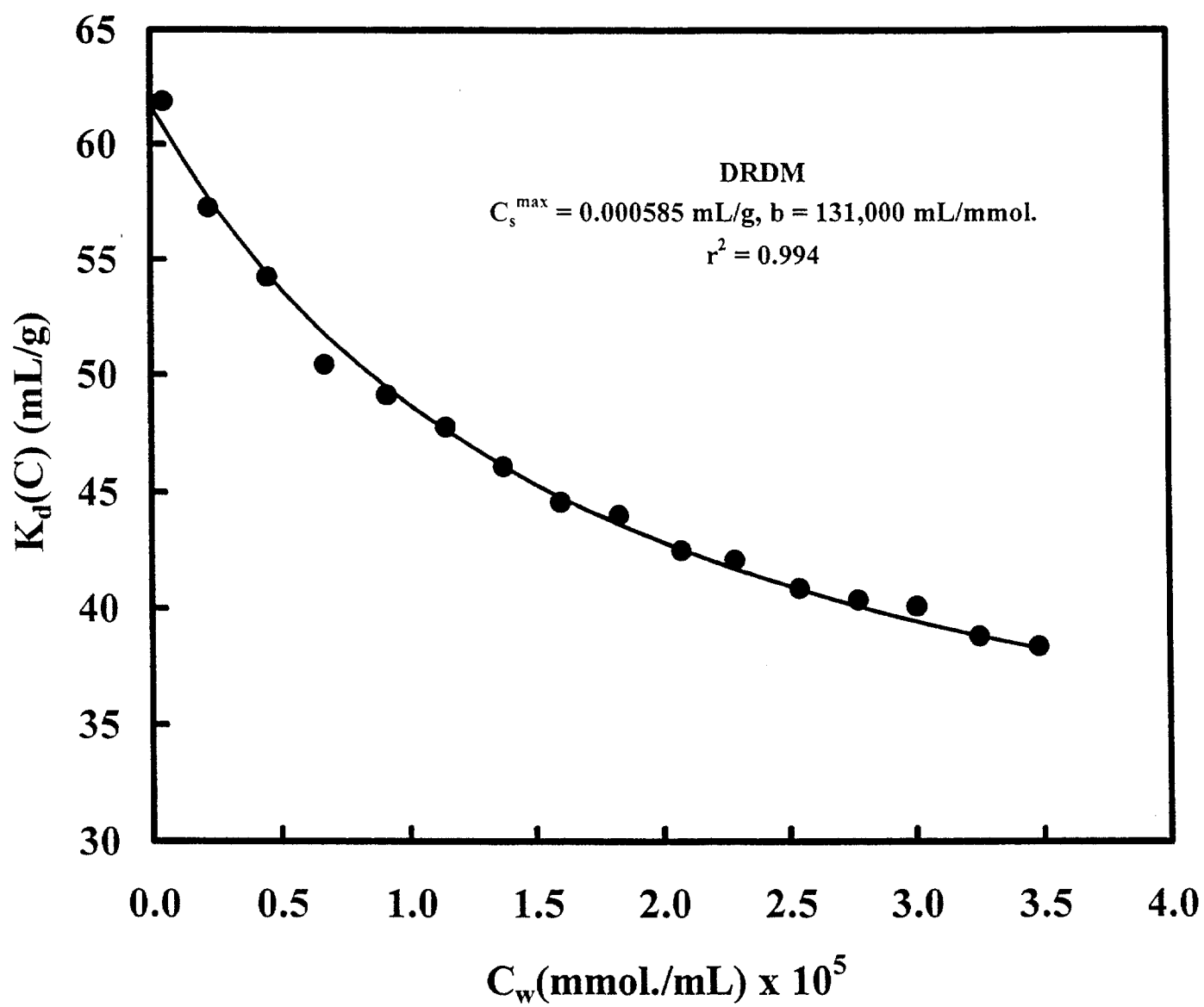


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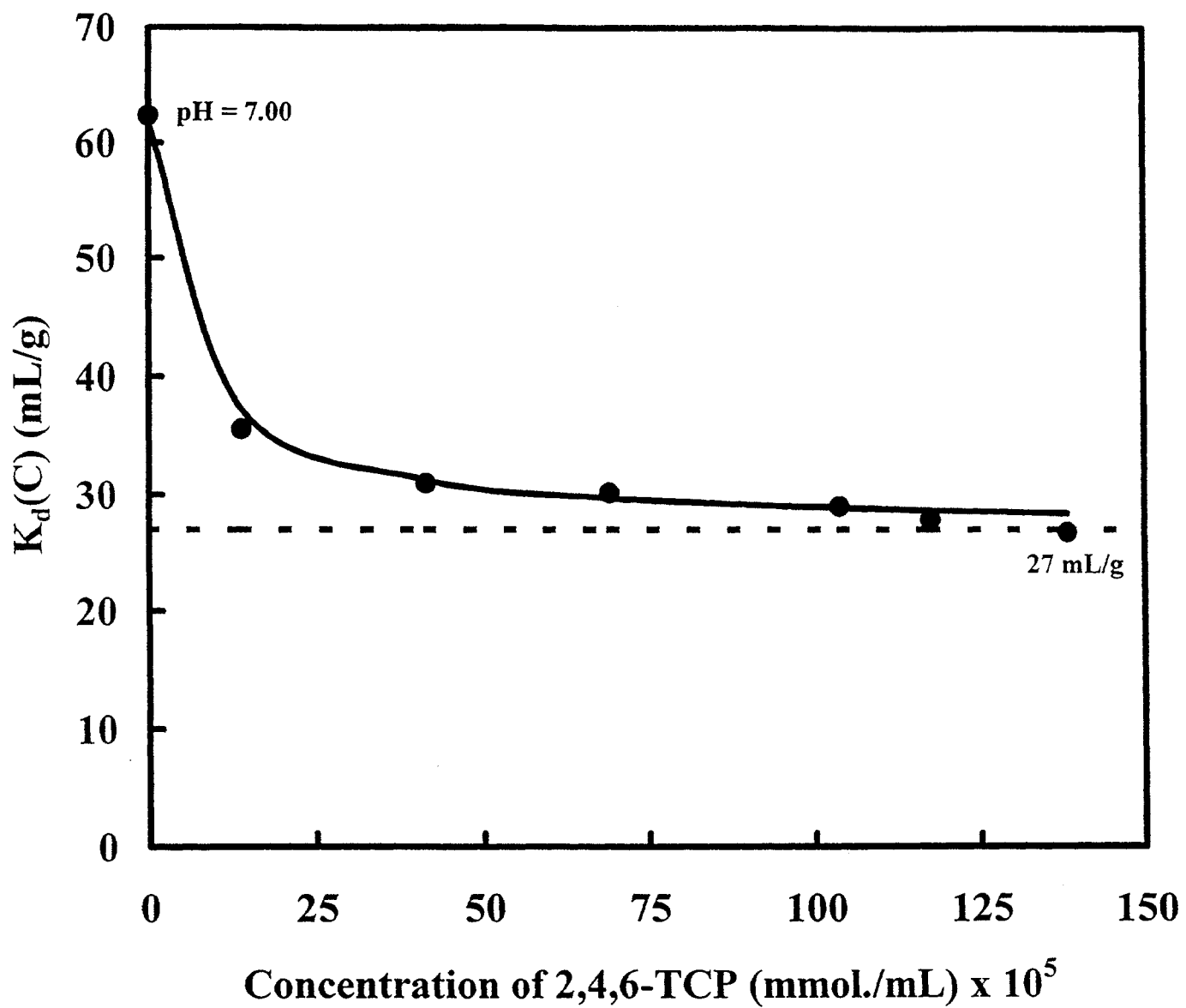


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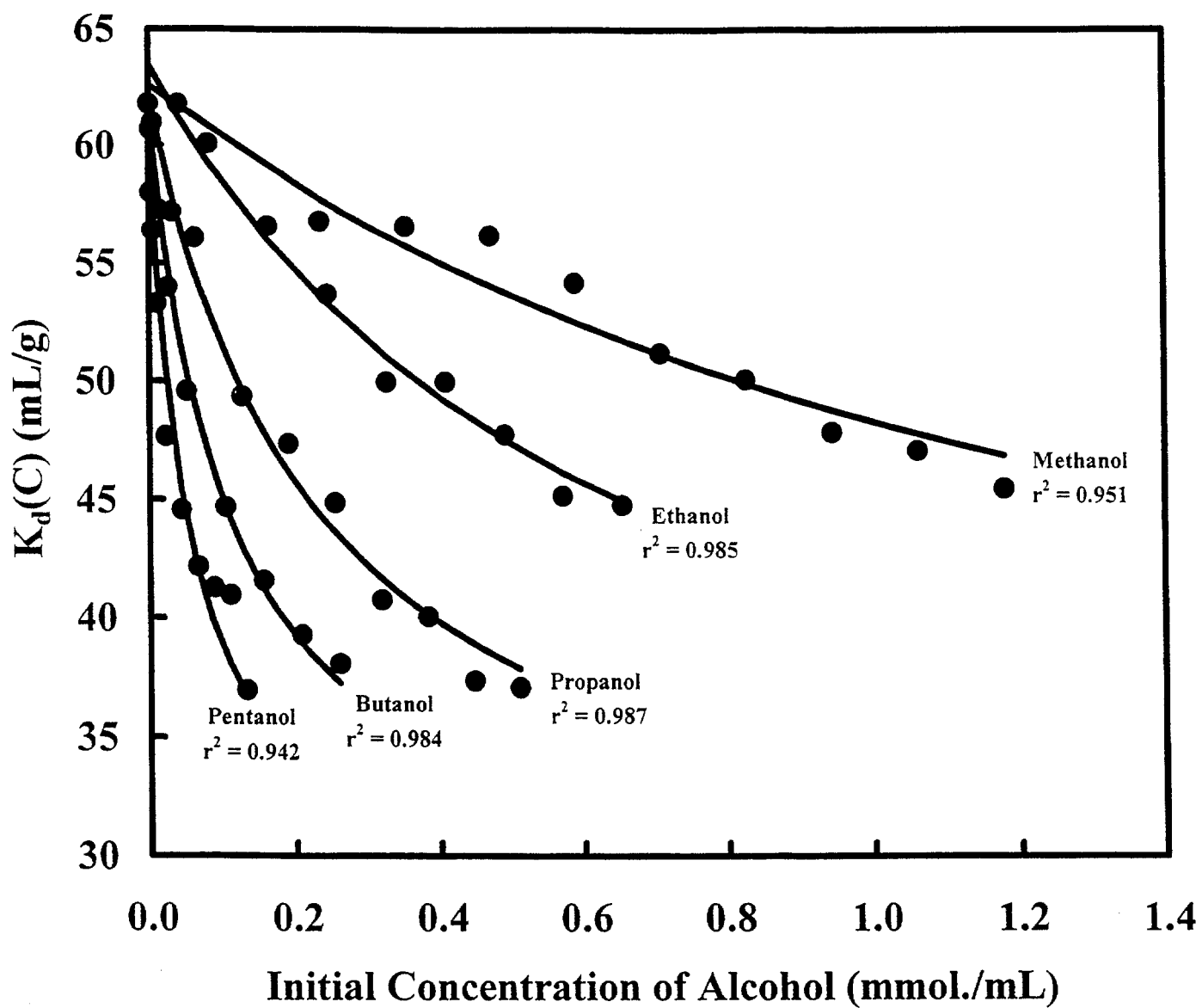


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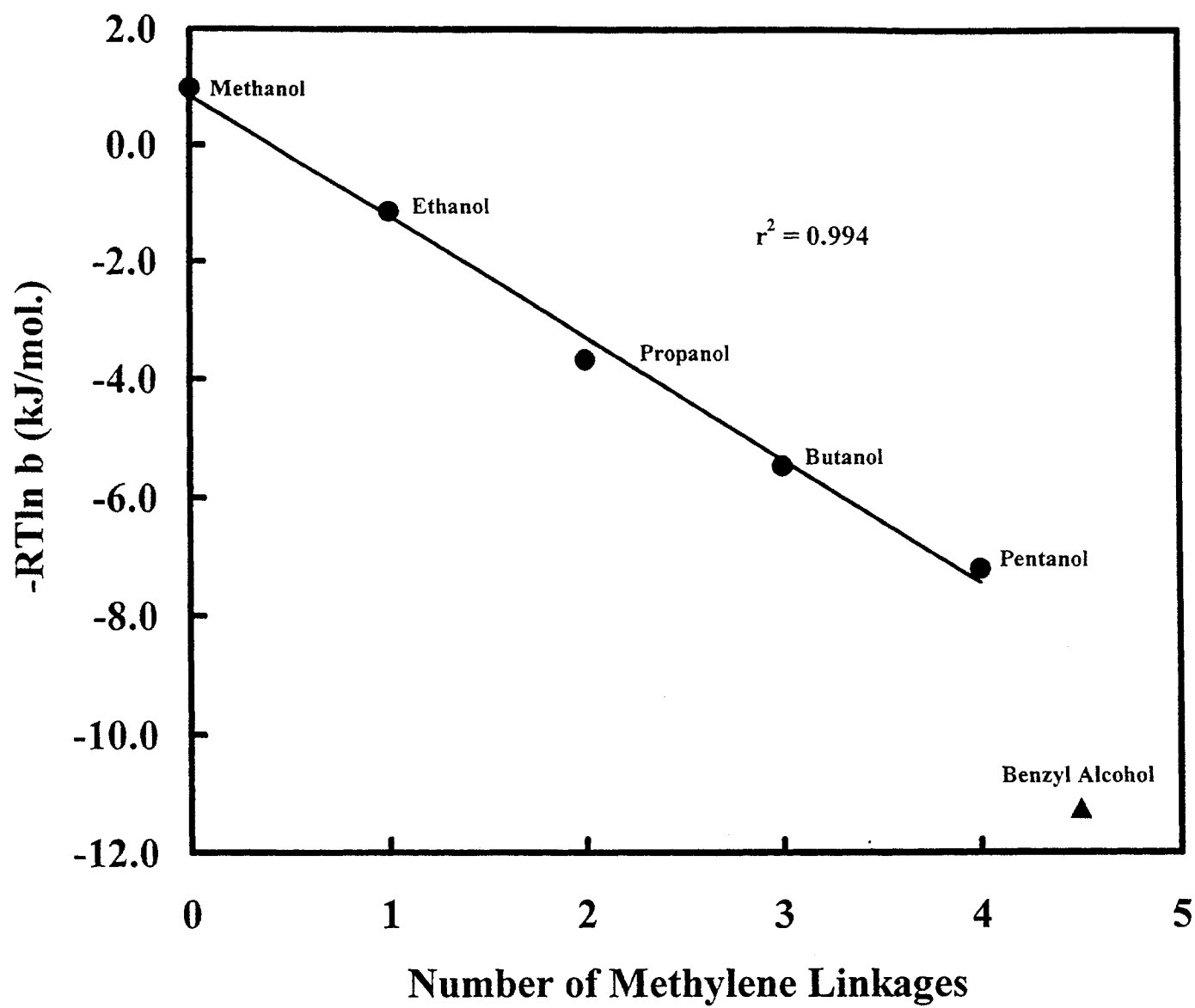


Fig. 8

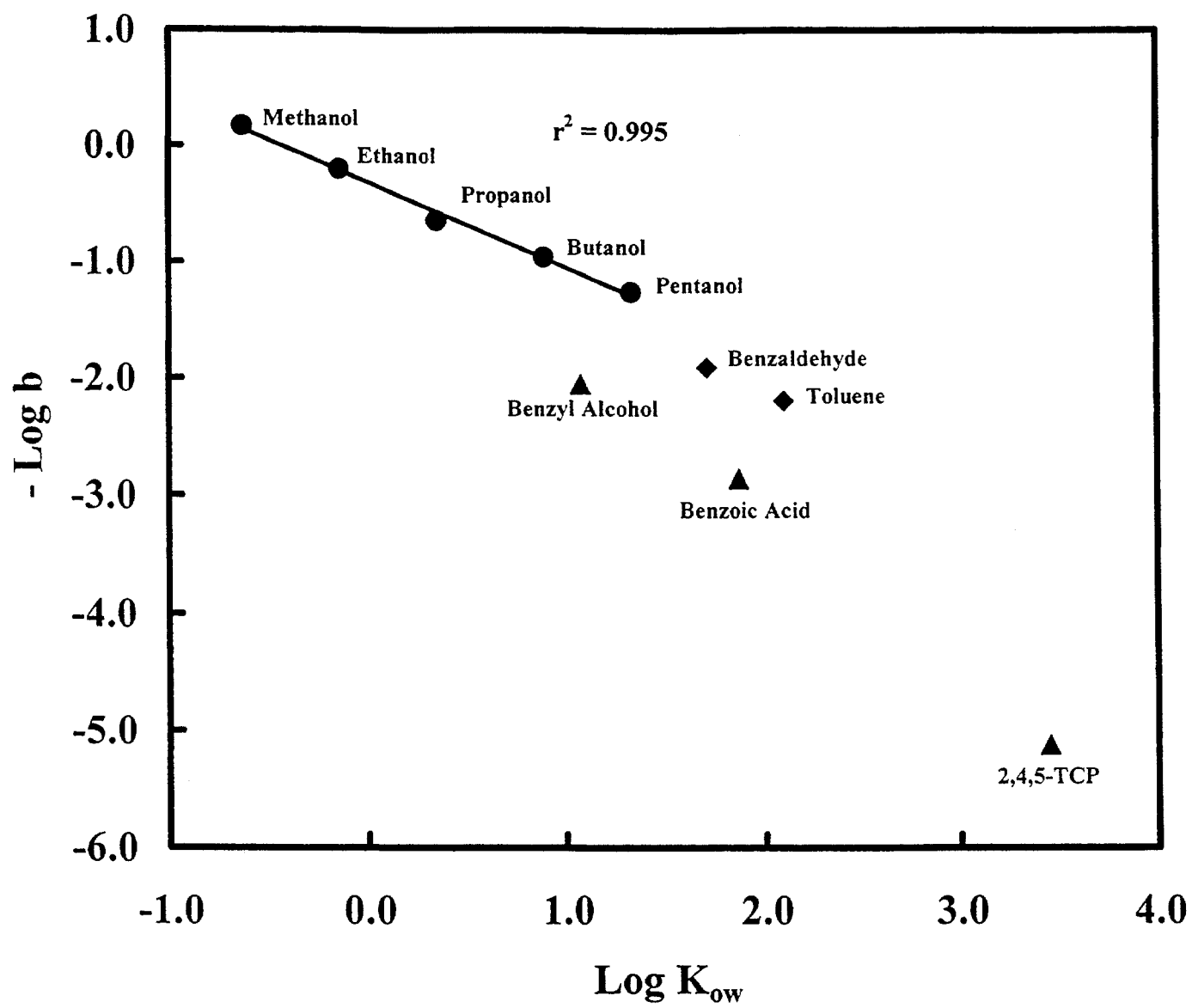


Fig. 9

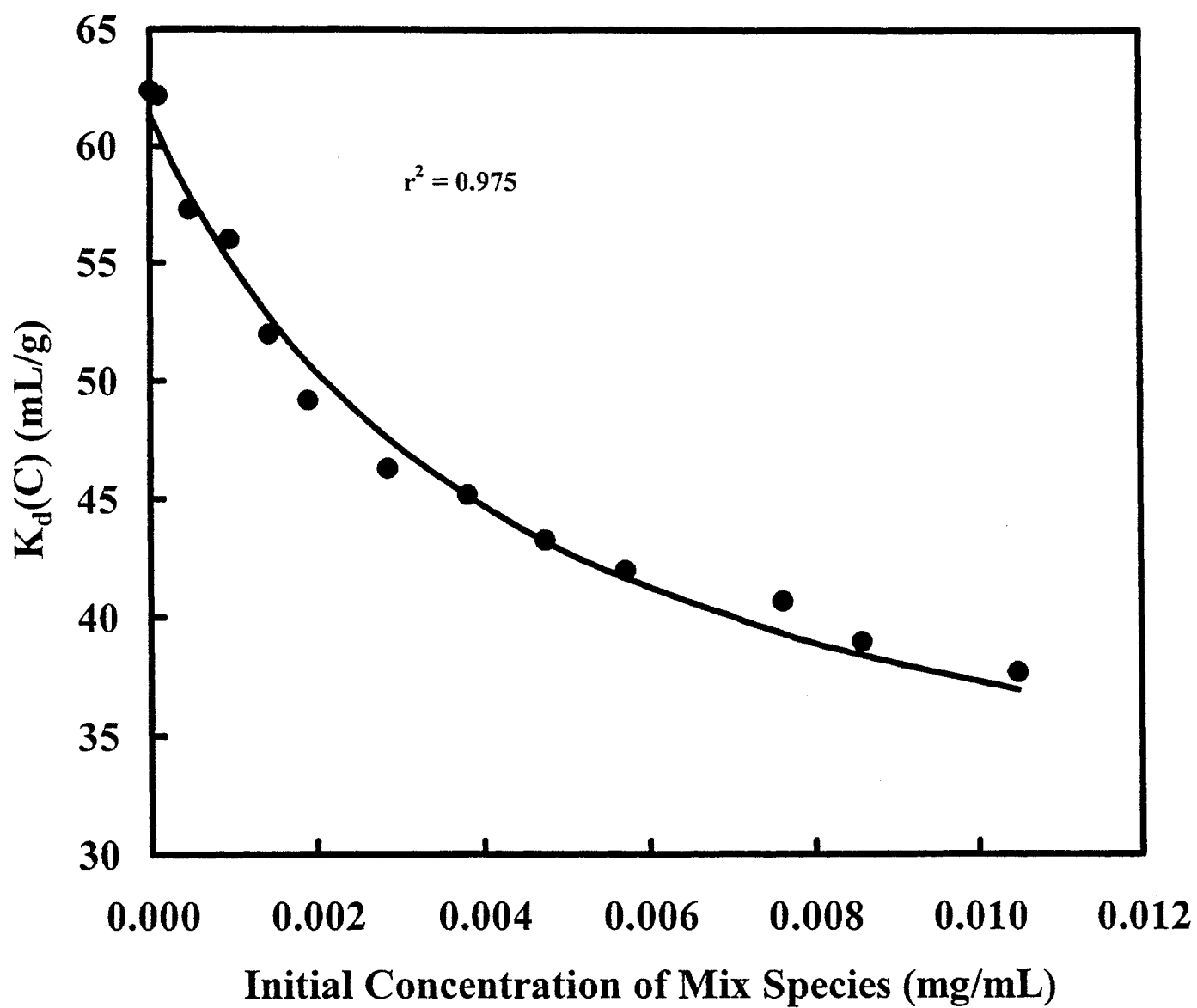


Fig. 10





